

VII.12 Low-Cost Spray Deposition for SOFC Manufacturing

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Phase One Objectives

In Phase I, NexTech Materials established the feasibility of low-cost manufacturing processes for solid oxide fuel cells that are highly flexible with respect to layer composition and morphology as well as cell geometry. The overall objectives of this proposed program are listed below:

- Demonstrate the applicability and versatility of aerosol spray deposition as a low-cost alternative to plasma spray and dip coating methods for the production of functional film layers for solid oxide fuel cells (SOFCs).
- Demonstrate the potential for process simplification by validation of low-temperature co-sintering of protocols of multilayer components including electrode interlayers, electrodes and electrolyte.
- Demonstrate the above processes on both anode- and cathode-supported SOFC designs that include different geometries and differing substrate pre-conditions.

Approach

The approach conducted at NexTech included the following salient points:

- Investigation of both aqueous and non-aqueous spray suspensions deposited by low-cost aerosol deposition techniques.
- Development of ink/slurry dispersion and manufacture techniques appropriate to large-scale manufacture and standard quality control protocol.
- Control of porosity/density and sinter activity of co-sintered materials by appropriate selection of surface area and particle size distribution, and green film density control by ink solids/organic loading.
- Analysis by microstructural assessment including optical and scanning electron microscopy (SEM) investigation.
- Electrolyte densification and defect analysis by vacuum leak testing.

Accomplishments

- Demonstrated aerosol deposition process that enables the uniform electrode and electrolyte coating of both anode- and cathode-supported SOFC tubular designs.
- Demonstrated a single-step deposition and co-firing regime that results in a dense electrolyte layer validated by Siemens-Westinghouse Power Corporation (SWPC).
- Demonstrated a full cell (electrodes + electrolyte) deposition and single co-fire protocol for anode-supported structure resulting in fully dense electrolyte microstructure between porous electrode films.
- Scaled the process to reproducibly coat tube lengths up to 60 cm.

Future Directions

The Phase I Program is complete. NexTech is currently seeking commercial partners for further development.

Introduction

The objective of this Phase I Small Business Innovation Research (SBIR) project was to demonstrate the feasibility of a low-cost aerosol spray process for the deposition of electrochemically active layers for solid oxide fuel cells. Currently, processes that include electrochemical deposition and plasma spray amongst others are being used for the production of the SOFC functional components. These processes are inherently expensive as they require considerable capital investment, use expensive precursors and require several thermal processing sequences for each layer in the multi-layered structure.

This project aimed to demonstrate that using the aerosol deposition method, a multi-layer structure could be formed using minimized thermal processing steps and that the microstructure of these layers could be optimized for electrochemical performance.

This project focused on two types of SOFC designs currently under development by Solid State Energy Conversion Alliance (SECA) team leaders: the cathode-supported tubular design of Siemens-Westinghouse Power Corporation and the tubular anode-supported design of Acumentrics.

Results

Initial attempts to produce dense electrolyte structures on SWPC fully sintered cathode tubes were based on aqueous solvent systems. The most promising results were obtained when slurries with low solids contents were utilized. This was due to the highly porous nature of the substrate that readily absorbed the water solvent and tended to prevent the flow, rearrangement and relaxation of the film on the substrate. It is expected that it was this ability of the substrate to rapidly extract solvent from the slurry that limited the packing density of the film and resulted in high drying stresses. As the SWPC tubes are fully sintered, there is no further shrinkage that occurs during electrolyte densification; therefore,

maximization of the film green density is critical. Our second approach utilized a non-aqueous solvent system, which has enabled a much higher slurry and film density to be achieved.

The drying rates of films deposited using the non-aqueous solvent system are controlled by volatilization of the solvent, which typically takes 15 minutes at a temperature of 100°C. After drying and approximately 5 minutes cooling, secondary layers can be applied with no observed detrimental interactions with the initial layers. During this stage of Phase I, subsequent film sintering temperatures of 1250-1350°C were investigated. In total, some 80 samples have been manufactured in lengths up to 45 cm for microstructural and gas leak analysis. Several samples with leak rates lower than can be detected by our apparatus have been supplied to SWPC for analysis.

Figure 1a demonstrates the greater utility of the non-aqueous system in depositing multiple films of varying composition. The backscatter image shows that the fine scale porosity near the electrolyte surface is associated with an electrochemically active cathode layer, a composite of lanthanum strontium manganese (LSM) and gadolinia-doped ceria (GDC)-10 powders. This layer was initially sprayed and dried, then immediately over-coated with the electrolyte layer. This type of multi-component coating was unachievable in the aqueous coating systems; intermediate calcination steps were required to maintain the integrity of the electrolyte and active electrode layers. The coating layers shown in Figure 1b were co-fired on the dead-sintered tube at 1300°C for two hours. Top-down views of the two coating surfaces revealed the improved quality the interlayer material produced in the electrolyte by moderating the surface roughness of the as-produced tube.

Based on the interlayer results achieved in Figure 1, the logical extension of the approach was to incorporate anode layer deposition and co-sintering to eliminate as many firing steps as possible. While this approach has yet to be demonstrated on the

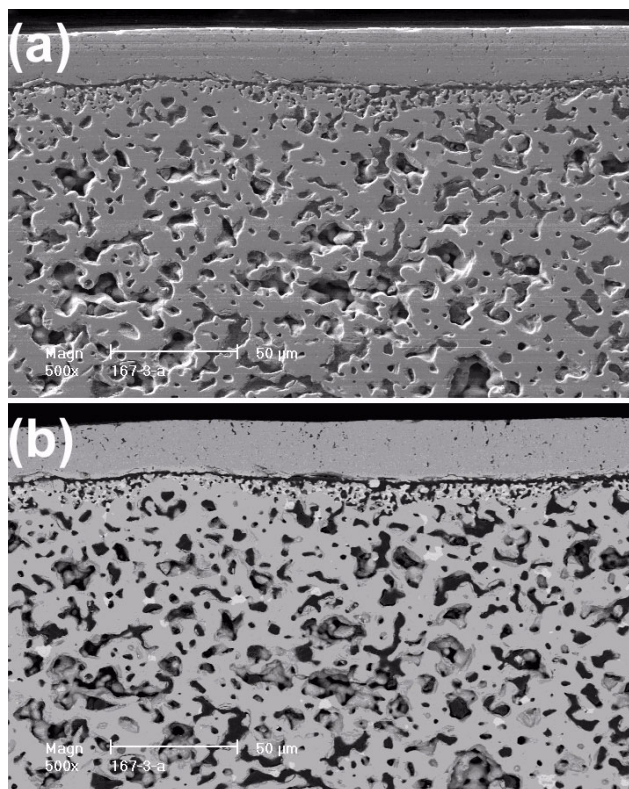


Figure 1. Zirconia-coated sample with LSM/GDC interlayer sintered at 1350°C. The picture on the top (a) is a secondary electron image; the picture on the bottom (b) is taken in backscatter mode.

SWPC tubes, it has been successfully completed in parallel work on anode supports. Figure 2 shows an aerosol-coated anode tube in which the interlayer and co-sintering processes have been taken to the next level of complexity. The tube shown in Figure 2 has four layers applied to the initial surface. An active anode layer, electrolyte, active cathode and current-carrying cathode layer have been applied and all sintered in a single step.

Conclusions

The technical achievement from this Phase I SBIR project is the demonstration of the feasibility of the aerosol spray deposition process for the producing electrochemically active layers in a solid oxide fuel cell. In addition to producing dense electrolyte films on SWPC cathode support tubes, greater levels of cell fabrication and process integration have been demonstrated on anode-supported tubes provided by Acumentrics, thereby

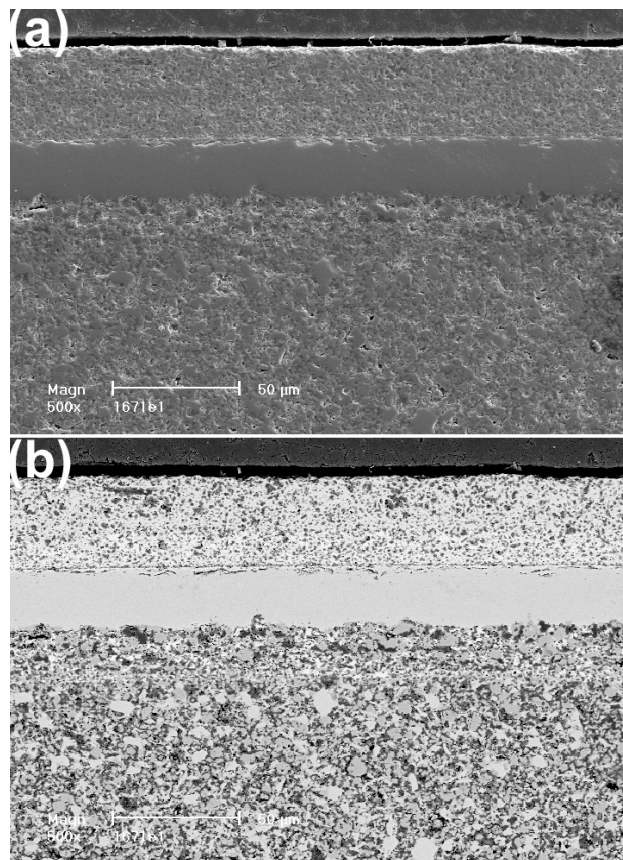


Figure 2. Zirconia-coated NiO-YSZ anode tube with active-anode interlayer, active cathode and current collector cathode layer, sintered at 1350°C. The picture on the top (a) is a secondary electron image; the picture on the bottom (b) is taken in backscatter mode.

demonstrating the applicability of the process multiple designs. In Phase I, a range of electrolyte spray formulations have been evaluated, improving coating deposition while maintaining low cost and low environmental impact. Alternative solvents have provided enhanced utility of the spray process and provided the opportunity for sequential depositions without intermediate calcination steps.

The successful manipulation of ink formulation for each of the functional layers, including electrode interlayer, current collectors and electrolyte, has resulted in the demonstration of a single sintering procedure for the electrochemical system for anode-supported cells. Co-firing temperatures as low as 1250°C appear to be feasible using this novel coating system.